A COLLOCATION-BASED MULTI-CONFIGURATION TIME-DEPENDENT HARTREE METHOD FOR COMPUTING VIBRATIONAL SPECTRA

ROBERT WODRASZKA, TUCKER CARRINGTON, *Department of Chemistry, Queen's University, Kingston, ON, Canada.*

It is possible to compute vibrational spectra using the Heidelberg implementation of the multi-configuration time-dependent Hartree method. However, the Heidelberg program can only be used if the potential energy surface is a sum of products (SOP). I shall present a new collocation-based MCTDH approach that can be used with general potential energy surfaces. This is imperative if one wishes to compute very accurate spectra. Collocation obviates the need for quadrature and facilitates using complicated kinetic energy operators. When the basis is good, the accuracy of collocation solutions to the Schroedinger equation is not sensitive to the choice of the collocation points. We test the collocation MCTDH equations by showing that they can be used to compute accurate vibrational energy levels of CH_3. MCTDH, with or without collocation, uses a direct-product basis. I shall demonstrate that by using so-called hierarchical basis functions, it is possible to both benefit from the advantages of collocation and prune the MCTDH basis. These new computational tools will make it possible to use MCTDH-type methods to compute very accurate spectra.